
Hanford Technical Assistance Project

Extension of Rocky Flats Equivalency for Lower Temperature Stabilization of Chloride-Bearing Pu Oxide

Purposes of Workshop

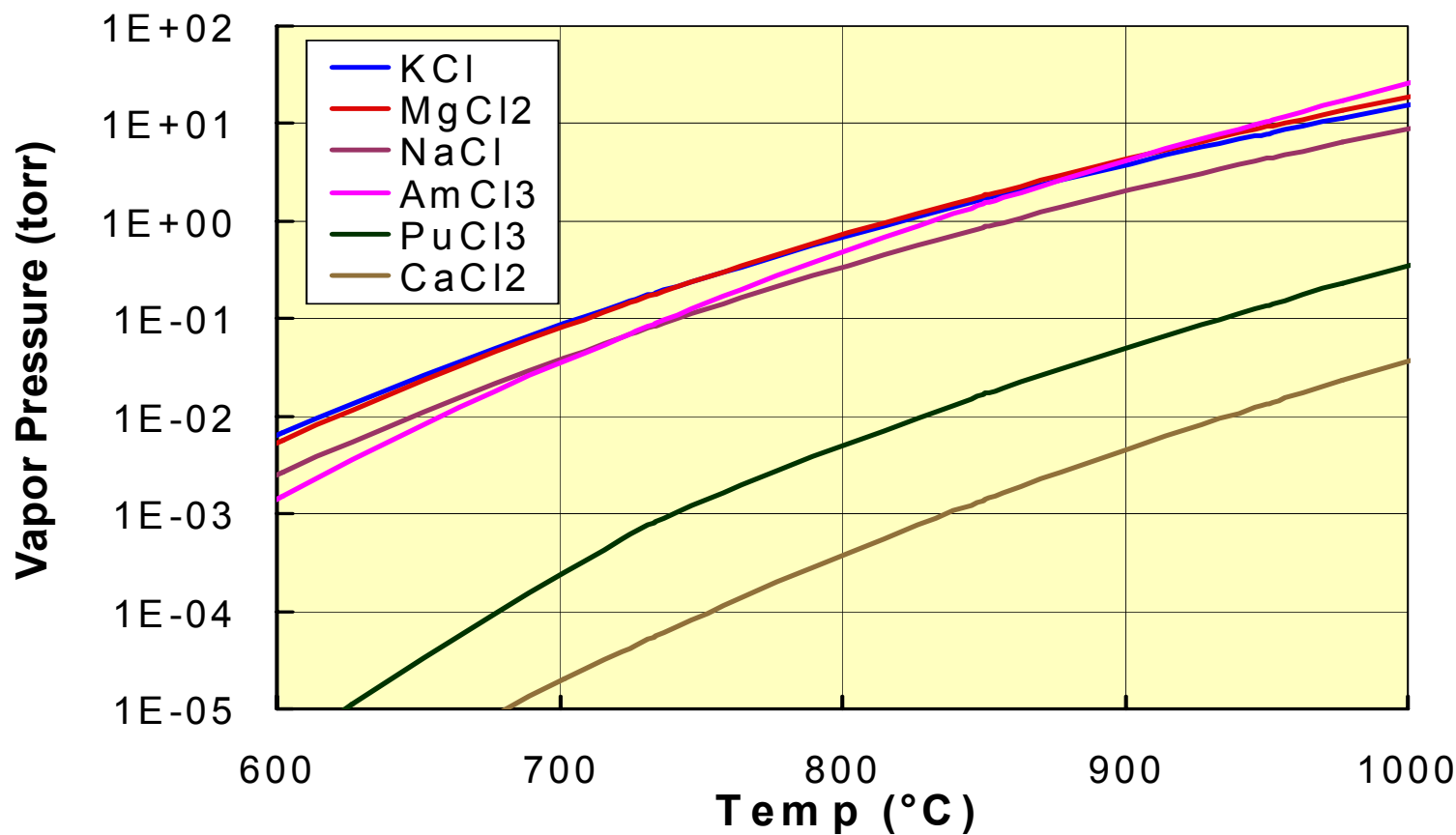
- **Review categories of Hanford Pu material with chloride**
- **Discuss chloride wash option**
- **Determine how lower calcination T (800 °C) can be defended**
- **If needed, define logic for lower T**
- **Define path forward; assign actions**

Purposes of Calcination

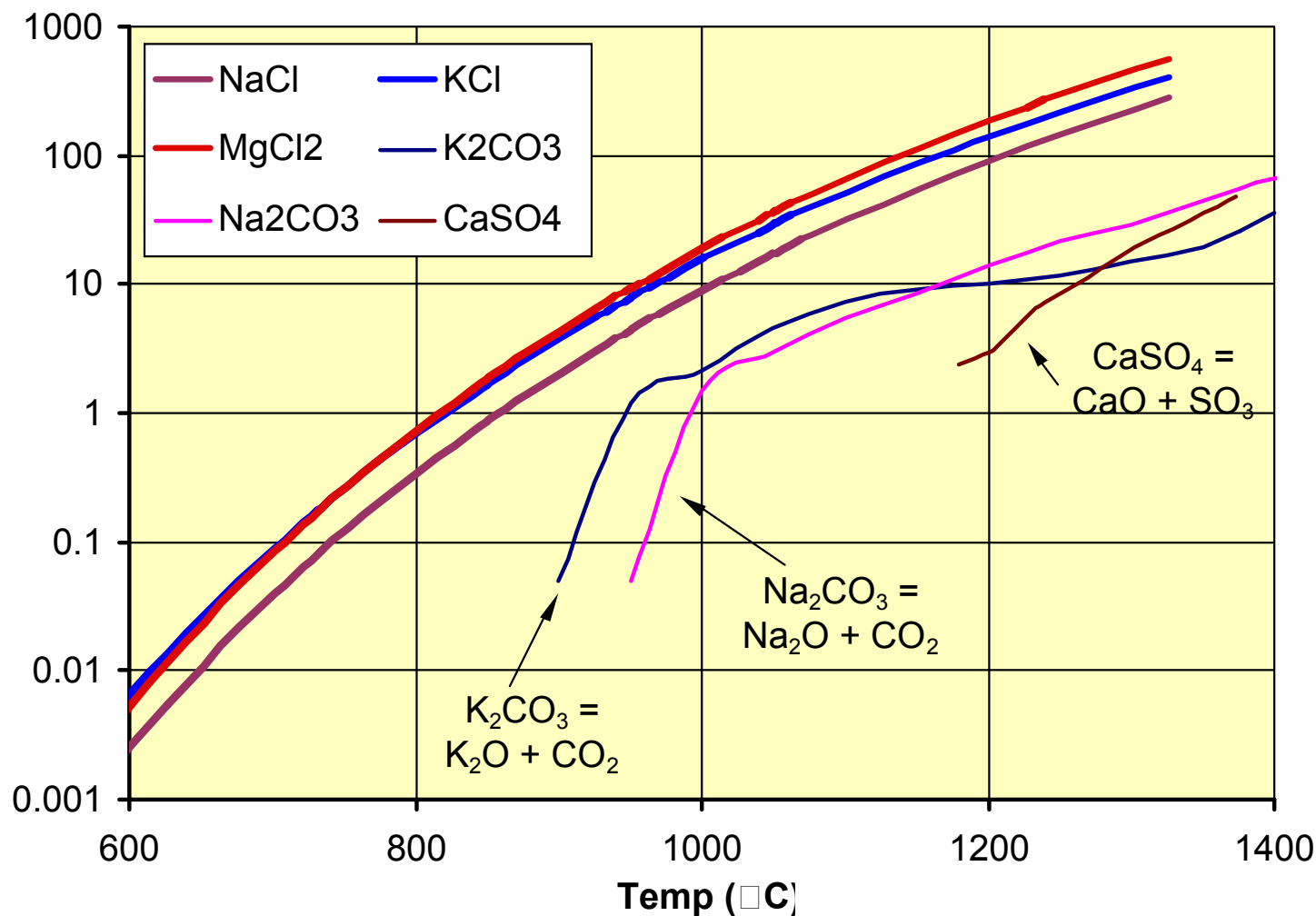
- **Eliminate reactive materials (metal/sub-stoichiometric oxides)**
- **Eliminate organic materials**
- **Reduce water content (and water-producing species) to <0.5 wt%**
- **Minimize potential for readsorption of water above 0.5 wt%**
- **Stabilize any other potential gas-producing constituents**

Chloride Vapor Pressures

200 °C reduction of stabilization temperature reduces chloride volatility by a factor >20



Calcination of Oxyanion Salts



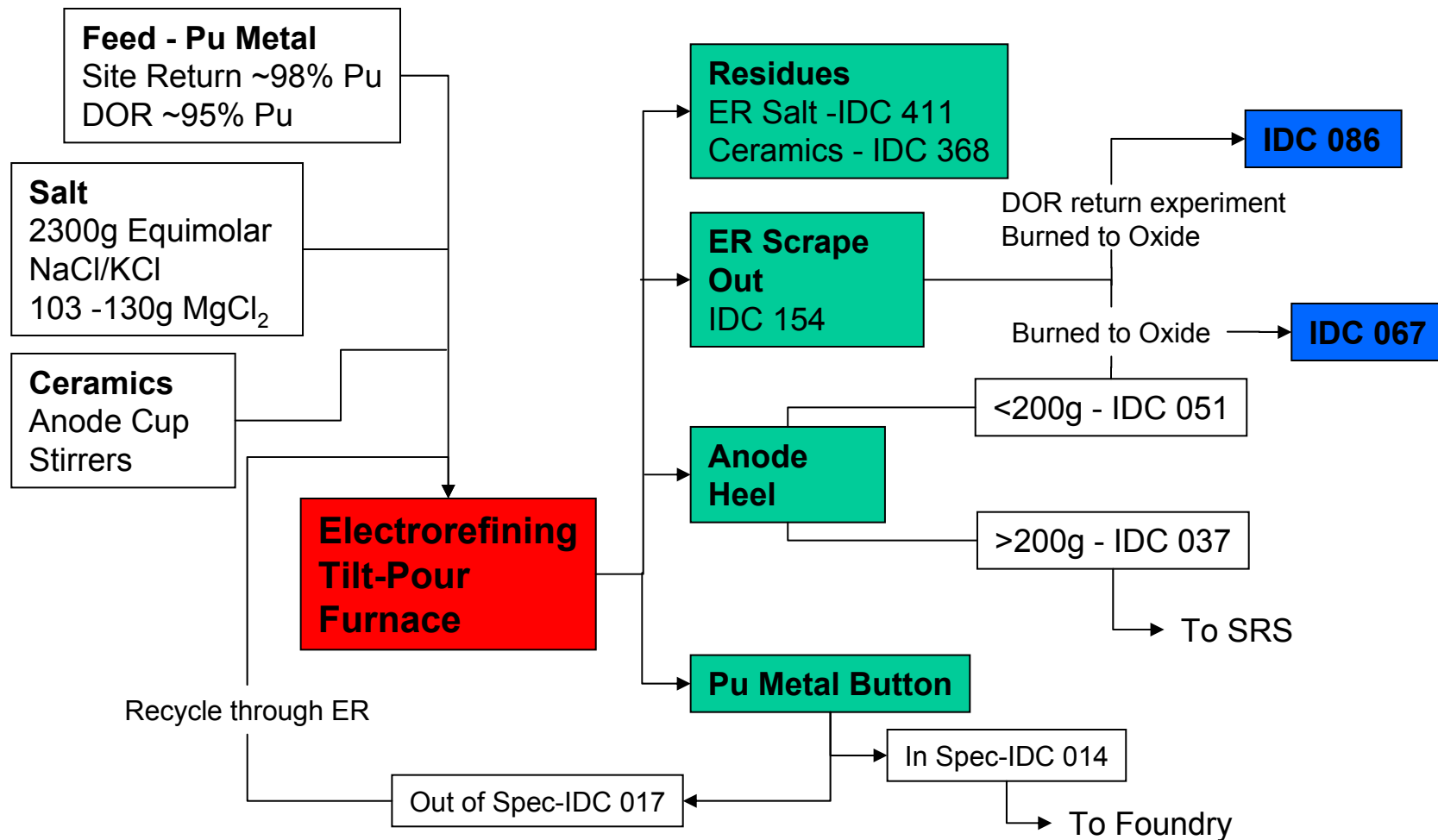
Changing the Calcination Temperature

- **Requires either:**
 - Modification of DOE STD 3013, or
 - Exemption from DOE STD 3013, or
 - **Equivalency to DOE STD 3013**
- **Technical Case for Either Option:**
 - Must show that all calcination purposes are adequately addressed at the lower calcination T, or
 - Calcination purposes that cannot be addressed either do not mitigate a significant risk, or can be managed via surveillance and monitoring programs

The Logic of Equivalency

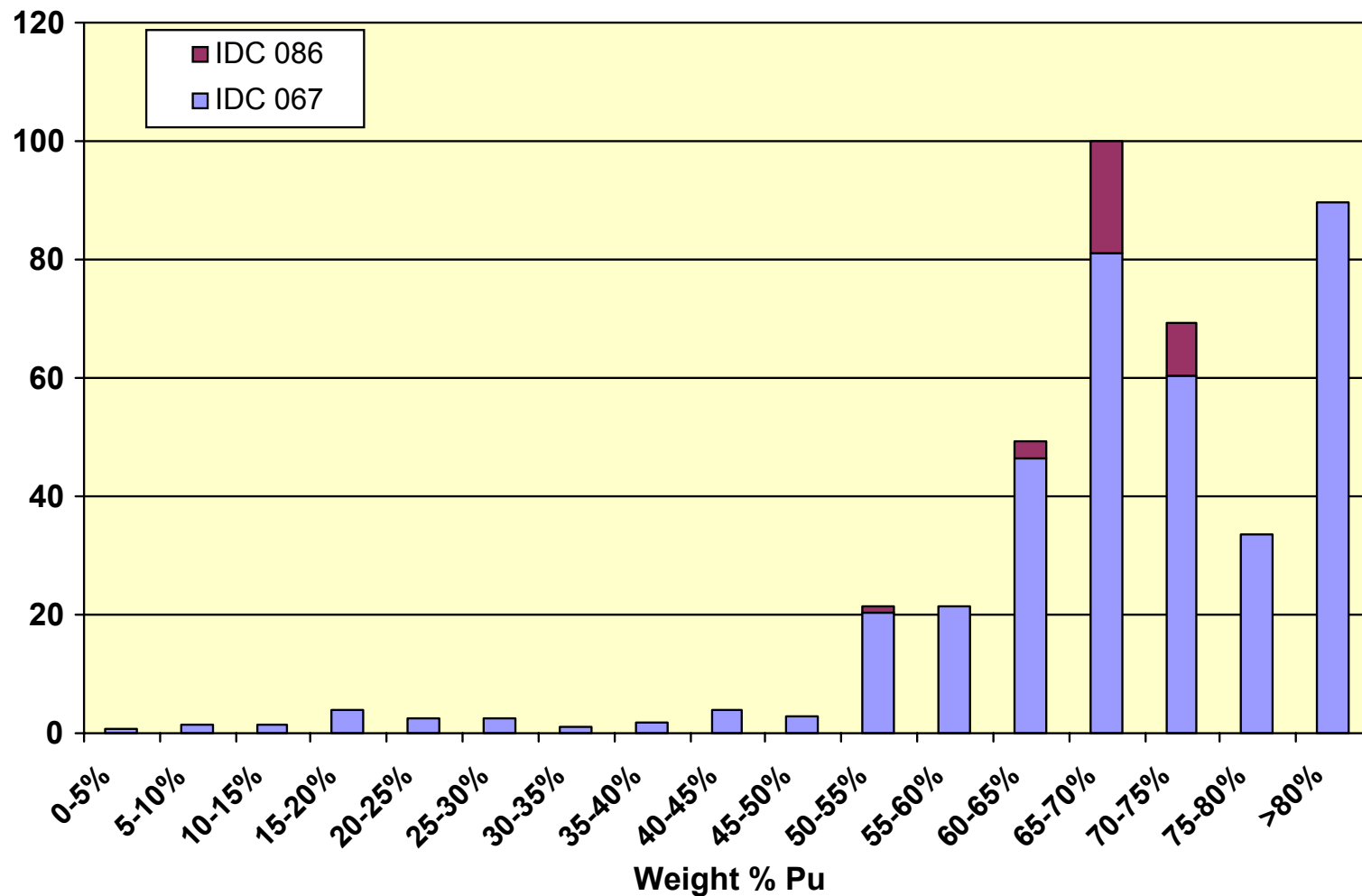
- **Report must argue, for any potential constituent of concern, that:**
 - It isn't there, *or*
 - It will be gone by 750 °C, *or*
 - It will still be there at 950 °C, *or*
 - It won't make a difference to gas generation or corrosion anyway, and
 - Any threat to a container would be detected

Electrorefining Process Flow Diagram



Pu Content of ER Oxides

Rocky Flats Electrorefining Oxide



Major Constituents of RFETS ER Oxides

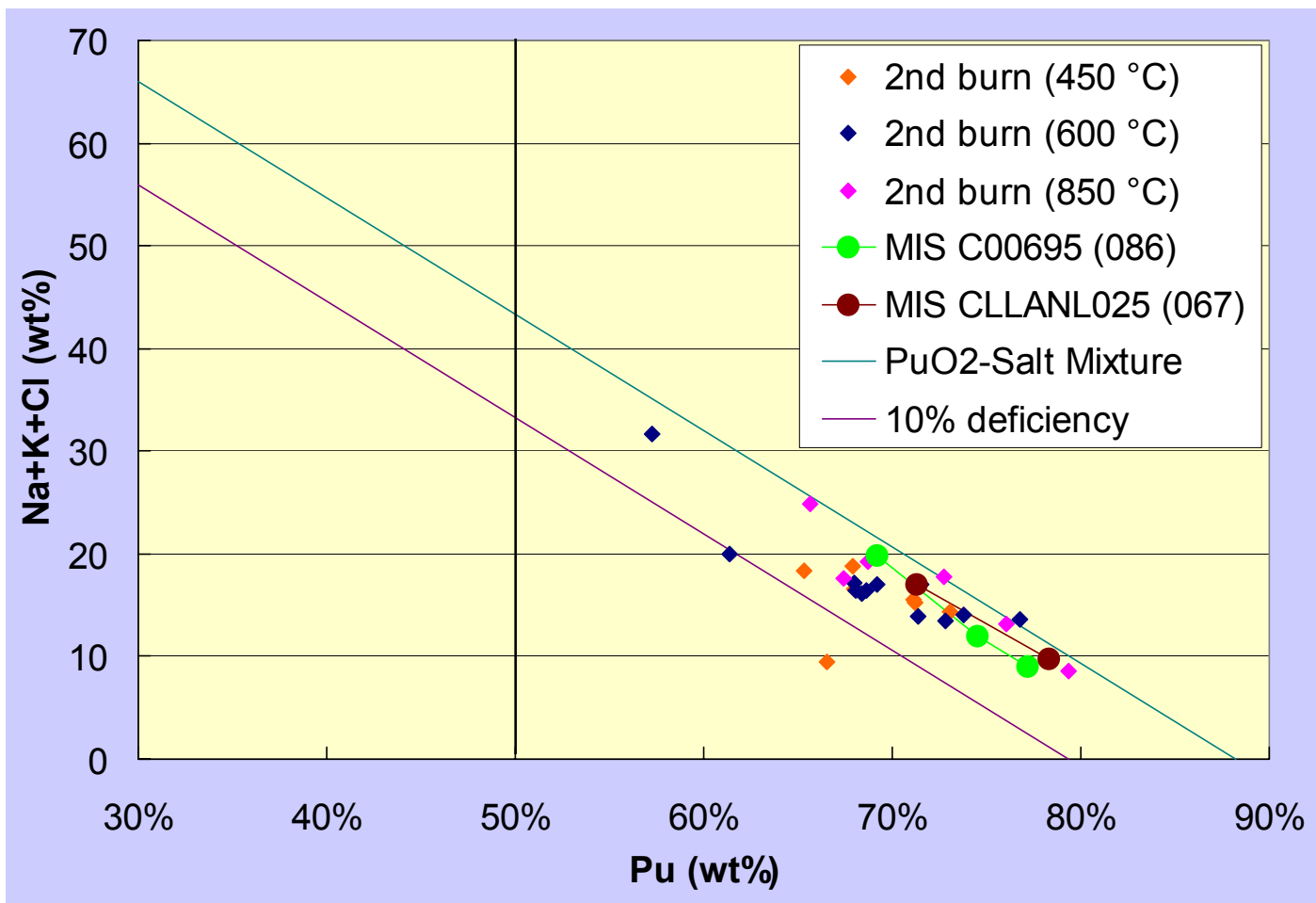
IDC	067		086		
MIS Item Number	CLLANL025 (HL025)		C00695 (T0695)		
Calcination	As Received	950 °C	As Received	800 °C	950 °C
Pu (wt%)	71.30	78.30	69.17	74.48	77.15
O* (wt%)	9.54	10.48	9.26	9.97	10.33
Cl (wt%)	10.00	5.90	9.00	7.00	5.50
K (wt%)	5.12	2.90	3.47	2.76	1.75
Na (wt%)	1.96	1.01	7.43	2.22	1.77
Mg (wt%)	0.55	0.38	2.00	0.94	0.72
Trace Constituents (wt%)	1.33	1.37	0.85	1.14	1.49
Sum* (wt%)	99.79	100.33	101.17	98.49	98.69

* Calculated based on all Pu as PuO₂

Trace Constituents of RFETS ER Oxides

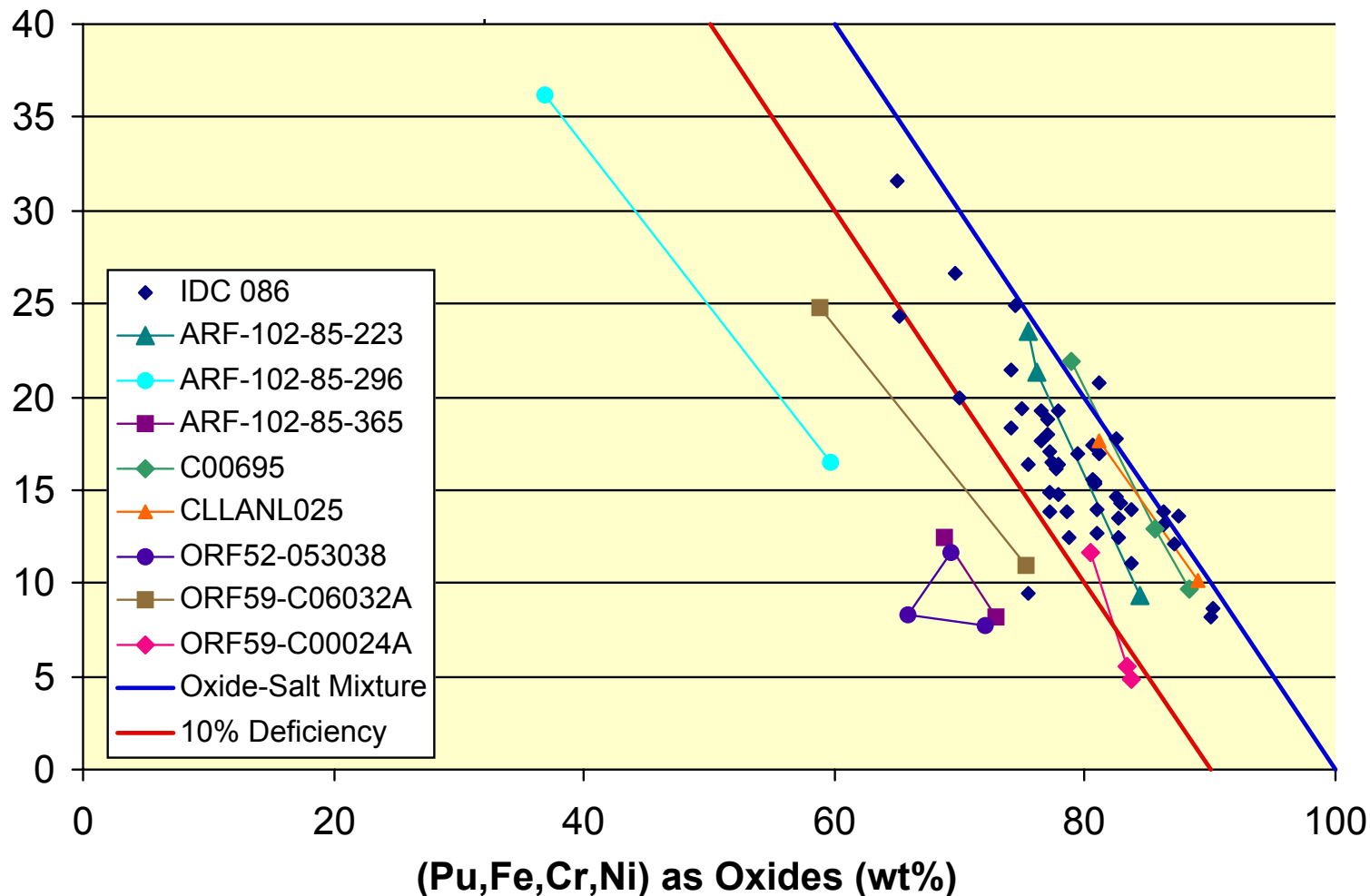
IDC	067		086		
MIS Item Number	CLLANL025 (HL025)		C00695 (T0695)		
Calcination	As Received	950 °C	As Received	800 °C	950 °C
C (wt%)	0.02	0.01	0.01	0.02	0.01
S (wt%)	<0.0084	0.02	0.08	0.03	0.18
F (wt%)	0.14	0.06-0.11	0.03	0.03	0.03
Al (wt%)	0.34	0.34	0.02	<0.003	<0.0062
Si (wt%)	0.38	0.43	<0.16	<0.16	<0.16
Ni (wt%)	0.09	0.05	0.27	0.71	0.39
Fe (wt%)	0.04	0.04	0.08	0.07	0.25
Ca (wt%)	.01	.01	.04	.02	.15
Am (wt%)	0.18	0.20	0.10		0.24
Other trace constituents	0.12	0.16	0.06	0.10	0.08
Sum (wt%)	1.33	1.32-1.37	0.85	1.14	1.49

Major Constituents of IDC 086



Major Constituents of Cl-bearing Oxides

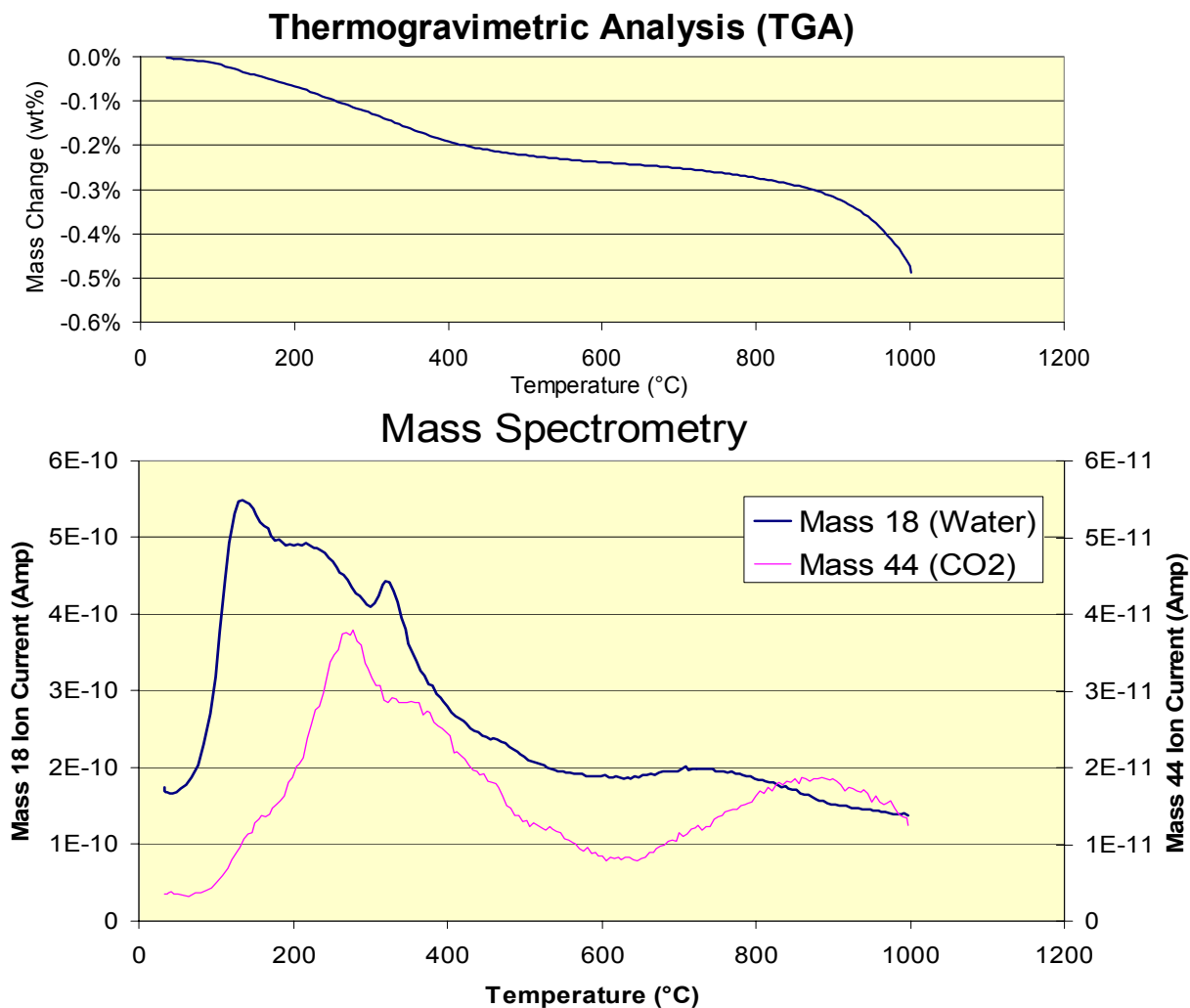
Chloride-Bearing Oxide Mass Balance



TGA Peak Temperature

- **Reduction of TGA peak temperature requires demonstration that:**
 - No moisture comes off above peak T, or
 - Reasonable bound can be placed on amount released above peak T
 - Total measurement uncertainty remains low enough

Moisture Content of C00695 (T0695)



Phase chemistry of impure oxide

	Material As Received by MIS	After 750°C Stabilization	After 950°C Stabilization
<i>Major Phases</i>			
PuO ₂	>34-100 wt %	Slight increase possible	Slight increase
NaCl	>0-38 wt %	Slight decrease expected	Significant decrease expected
KCl	>0-39 wt %	Slight decrease expected	Significant decrease expected
<i>Minor Chloride Phases</i>			
PuCl ₃	Potentially present	Probably absent	Probably absent
PuOCl	Potentially present	Potentially present	Potentially present
KMgCl ₃	Potentially present	Potentially present	Potentially present
Na ₂ MgCl ₄	Potentially present	Potentially present	Potentially present
MgCl ₂	Probably absent	Probably absent	Probably absent
<i>Residual Metal Phases</i>			
Pu metal	Potentially present	Potentially present	Potentially present
Mg metal	Potentially present	Potentially present	Potentially present
<i>Other Minor Phases</i>			
Na ₂ O	Potentially present	Probably absent	Probably absent
K ₂ O	Potentially present	Probably absent	Probably absent
MgO	Potentially present	Potentially present	Potentially present
NaOH	Probably absent	Probably absent	Probably absent.
Na ₂ CO ₃	Probably absent	Probably absent	Probably absent.
KOH	Probably absent	Probably absent	Probably absent.
K ₂ CO ₃	Probably absent	Probably absent	Probably absent.
Mg(OH) ₂	Potentially present	Potentially present	Potentially present
MgCO ₃	Potentially present	Potentially present	Potentially present
Adsorbed H ₂ O/OH ⁻	Potentially present	<0.2 wt % expected	<0.2 wt % expected
Adsorbed CO ₂ /CO ₃ ⁻²	Potentially present	<0.2 wt % expected	<0.2 wt % expected

Building on the RFETS case

- **Reactive materials - argument appears OK**
- **Organic materials - should be OK**
- **Reduction of water content - RFETS data on ER Oxides for some materials**
- **Readsorption - concern about Mg salts?**
- **Gas-producing constituents - 94-1 review adequate?**